COVENANT UNIVERSITY
NIGERIA

TUTORIAL KIT
OMEGA SEMESTER

PROGRAMME: CHEMISTRY

COURSE: CHM 222

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1. Write chain propagation steps for the above bromination reaction.

$(CH_3)_3CH$ + Br_2 › $(CH_3)_3CBr$ + HBr

2. Consider the SN1 reaction of tert-butyl chloride with iodide ion:

$(CH_3)_3CCl + I^-$ › $(CH_3)_3CI + Cl^-$

If the concentration of iodide ion is doubled, the rate of forming tert-butyl iodide will:

(hint: consider mechanism, i.e. how is the product formed?)

(A) Double. (B) Increase 4 times. (C) Remain the same. (D) Decrease. (E) None of the above.

3. Separation efficiency is routinely determined by Separation factor; derive an expression showing the relationship between Separation factor, $S_{I,A}$ and recoveries, R_I and R_A

4. For the following reaction, the overall enthalpy change is:

CH $CH_3CH_2CH_2Br$ + HBr › $3CH_2CH_3$ + Br_2

(A) -12 kcal/mol (B) +12 kcal/mol (C) -300 kcal/mol (D) +300 kcal/mol (E) +15 kcal/mol

5. Mention four (4) important attributes of precipitation gravimetry.

6. A 0.6113 g sample of Dow metal, containing aluminum, magnesium, and other metals, was dissolved and treated to prevent interferences by the other metals. The aluminum and magnesium were precipitated with 8-hydroxyquinoline. After filtering and drying, the mixture of $Al(C_9H_6NO)_3$ and $Mg(C_9H_6NO)_2$ was found to weigh 7.8154 g. The mixture of dried precipitates was then ignited, converting the precipitate to a mixture of Al_2O_3 and MgO. The weight of this mixed solid was found to be 1.0022 g. Calculate the % w/w Al and % w/w Mg in the alloy. Given that AW of Al = 26.98 g/mol, Mg = 24.31 g/mol, C = 12.01 g/mol, N = 14.01 g/mol, O = 16.0 g/mol, H = 1.008 g/mol

7. An impure sample of Na_3PO_3 weighing 0.1392 g was dissolved in 25 mL of water. A solution containing 50 mL of 3% w/v mercury(II) chloride, 20 mL of 10% w/v sodium acetate and 5 mL of glacial acetic acid was then prepared. The solution containing the phosphite was added dropwise to the second solution, oxidizing PO_3^{3-} to PO_4^{3-} and precipitating Hg_2Cl_2. After digesting, filtering, and rinsing, the precipitated

Hg_2Cl_2 was found to weigh 0.4320 g. Report the purity of the original sample as %w/w Na_3PO_3. Given that AW of Na = 22.99 g/mol, P = 30.97 g/mol, Hg = 200.5 g/mol, Cl = 35.45 g/mol

8. Which of the following alkyl halides would undergo SN2 reaction most rapidly?
(A) CH_3CH_2-Br (B) CH_3CH_2-Cl (C) CH_3CH_2-I (D) CH_3CH_2-F (E) they react at the same rate

9. Write a short note on each of the following types of impurity in gravimetric precipitation
(i) Inclusions (ii) Occlusions (iii) Surface adsorbates

10. The following table shows selected gravimetric methods for inorganic anions based on precipitation:

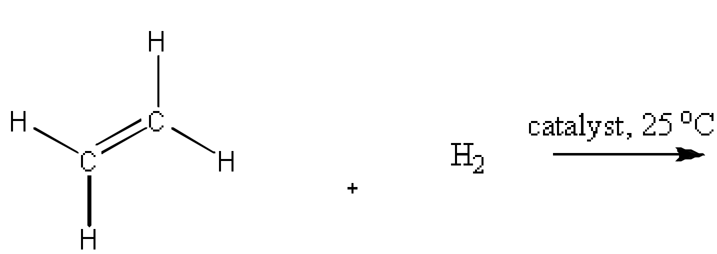
Analyte	Precipitant	Precipitate Formed	Precipitate Weighed
CN^-	$AgNO_3$	?	?
I^-	$AgNO_3$	?	?
Br^-	$AgNO_3$	?	?
Cl^-	$AgNO_3$	?	?
ClO_3^-	$FeSO_4/AgNO_3$	?	?
SCN^-	$SO_2/CuSO_4$	?	?

11. The bond dissociation energy is the amount of energy required to break a bond
a) so as to produce the more stable pair of ions
b) heterolytically c) homolytically d) via hydrogenation e) none of the above

12. The following equation shows the bromination of methane:
CH_4 + Br › CH_3Br + HBr

1) Propose a mechanism (initiation and propagation steps) to account for the product formation. Label the steps as A, B, C... and calculate the DH° for each step.

At the room temperature (25 °C), ethene can be hydrogenated (add one mole of H_2 to the double bond) to give ethane in the presence of a catalyst, as shown below:



13. Calculate the equilibrium constant for this reaction if there is sufficient data. If there is not enough data to allow for such calculation, simply state so.

14. Predict the sign of this DS° for this reaction. Briefly explain your reasoning.

15. Predict the sign of DH° for this reaction. Explain briefly how you arrive at this conclusion.
DG°=DH°-TDS°. It then follows that DH° for this reaction is negative.

16. Given the bond dissociation energies below (in kcal/mol), calculate the overall DH° for the following reaction:

$(CH_3)_3CH$ + Br_2 › $(CH_3)_3CBr$ + HBr

$(CH_3)_3C$-H	91
$(CH_3)_3C$-Br	65
Br-Br	46
H-Br	88
CH_3-Br	70

17. Which of the following alkyl halides would undergo SN2 reaction most rapidly?
(A) CH_3CH_2-Br (B) CH_3CH_2- Cl (C) CH_3CH_2-I (D) CH_3CH_2-F (E) they react at the same rate

18. Which of the following alkyl halides would you expect to give the highest yield of substitution product (SN_2) with $CH_3CH_2O^-Na^+$?
   A. $CH_3CH_2CH_2CH_2CH_2$ Br
   B. $CH_3CH_2CH_2CH$ $BrCH_3$
   C. $CH_3CH_2CCH_3BrCH_3$

19. Derive an expression to show that an interference will not pose a problem in the determination of an analyte when the product of its concentration and the selectivity coefficient is significantly smaller than the analyte's concentration. Hint: $S_{sample} = k_A C_A$

SOLUTIONS

1. (a) In the absence of interferent, the relationship between the sample's signal,

   $S_{sample} = k_A C_A$ ……. (i)

   where k_A is the analyte's sensitivity. In the presence of an interferent, equation (i) becomes $S_{Sample} = k_A C_A + k_I C_I$ ……………… (ii)

where k_I and C_I are the interferent's sensitivity and concentration respectively. A method's selectivity is determined by the relative difference in its sensitivity towards the analyte and interferent. If k_A is greater than k_I then the method is more selective for the analyte. The method is more selective for the interferent if k_I is greater than k_A. Even if a method is more selective for an interferent, it can be used to determine the analyte's concentration provided the interferent's contribution to S_{Samp} is significant. The selectivity coefficient, $K_{A,I}$, can be introduced as a means of characterizing a method's selectivity.

[illegible] ……… ([illegible])

Solving equations (ii) and (iii) for k_I

k [illegible]

[illegible] (iv)

2. In SN1 reaction, the rate is independent of the nucleophile involved since the nucleophile is not involved in the rate determining step.

   Thus the answer is C.

4. The key here is to understand how the heat of the reaction is related to bond dissociation energy (BDE) and the definition of BDE. Also it is essential to know that bond breaking requires energy.

   The answer is (A)

6. g $Al(C_9H_6NO)_3$ + g $Mg(C_9H_6NO)_2$ = 7.8154

$$g\ Al_2O_3 + g\ MgO = 1.0022$$

$$2 \times \text{moles } Al_2O_3 = \text{moles } Al(C_9H_6NO)_3$$

Converting from moles to grams and solving yields an equation relating the grams of Al_2O_3 to the grams of $Al(C_9H_6NO)_3$

[illegible]

$= 0.11096 \times$ [illegible]

For Mg we have

$$\text{Moles MgO} = \text{moles Mg(C}_9\text{H}_6\text{NO)}_2$$

[illegible]

$= 0.12893 \times$ [illegible]

Substituting the equations for g MgO and g Al_2O_3 into the equation for the combined weights of MgO and Al_2O_3 leaves us with two equations and two unknowns.

$$\text{g Al(C}_9\text{H}_6\text{NO)}_3 + \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.8154 \quad \text{.........} \ (1)$$

$$0.11096 \times \text{g Al(C}_9\text{H}_6\text{NO)}_3 + 0.12893 \times \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 1.0022 \ \ldots(2)$$

Multiplying the first equation by 0.11096 and subtracting the second equation

Gives

$$-0.01797 \times \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = -0.1350$$

which can be solved for the mass of $Mg(C_9H_6NO)_2$.

$$\text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.5125 \text{ g}$$

The mass of $Al(C_9H_6NO)_3$ can then be calculated using the known combined mass of the two original precipitates.

$$7.8154 \text{ g} - \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.8154 \text{ g} - 7.5125 \text{ g} = 0.3029 \text{ g Al(C}_9\text{H}_6\text{NO)}_3$$

Using the conservation of Mg and Al, the %w/w Mg and %w/w Al in the sample can now be determined as in Example 1, where AW is an atomic weight.

$\text{Moles Mg} = \text{moles Mg(C}_9\text{H}_6\text{NO)}_2$ $\qquad$ $\text{Moles Al} = \text{moles Al(C}_9\text{H}_6\text{NO)}_3$

[illegible]

$= \frac{[illegible]}{[illegible]}$ $= \frac{[illegible]}{[illegible]}$

$= 0.5841$ [illegible] $= 0.017$[illegible]

$\% [illegible] = \frac{[illegible]}{[illegible]} \times 100$ $\% [illegible] = \frac{[illegible]}{[illegible]} \times 100$

$\frac{[illegible]}{[illegible]} \times 100 = 95.55\%$ $\frac{[illegible]}{[illegible]} \times 100 = 2.91\%$

8. In Sn2 reaction, the nucleophile attacks from the back of the leaving group. The better the leaving group, the easier it is to leave (faster rate).

The answer is C since iodide ion is the best leaving group.

10.

Analyte	Precipitant	Precipitate Formed	Precipitate Weighed
CN^-	$AgNO_3$	AgCN	AgCN
I^-	$AgNO_3$	AgI	AgI
Br^-	$AgNO_3$	AgBr	AgBr
Cl^-	$AgNO_3$	AgCl	AgCl
ClO_3^-	$FeSO_4/AgNO_3$	$AgClO_3$	$AgClO_3$
SCN^-	$SO_2/CuSO_4$	AgSCN	AgSCN

14. Entropy measures degree of chaotic. Since two molecules combine to give one, the entropy has decreased, thus the change is negative.

17. In Sn2 reaction, the nucleophile attacks from the back of the leaving group. The better the leaving group, the easier it is to leave (faster rate). The answer is C since iodide ion is the best leaving group.